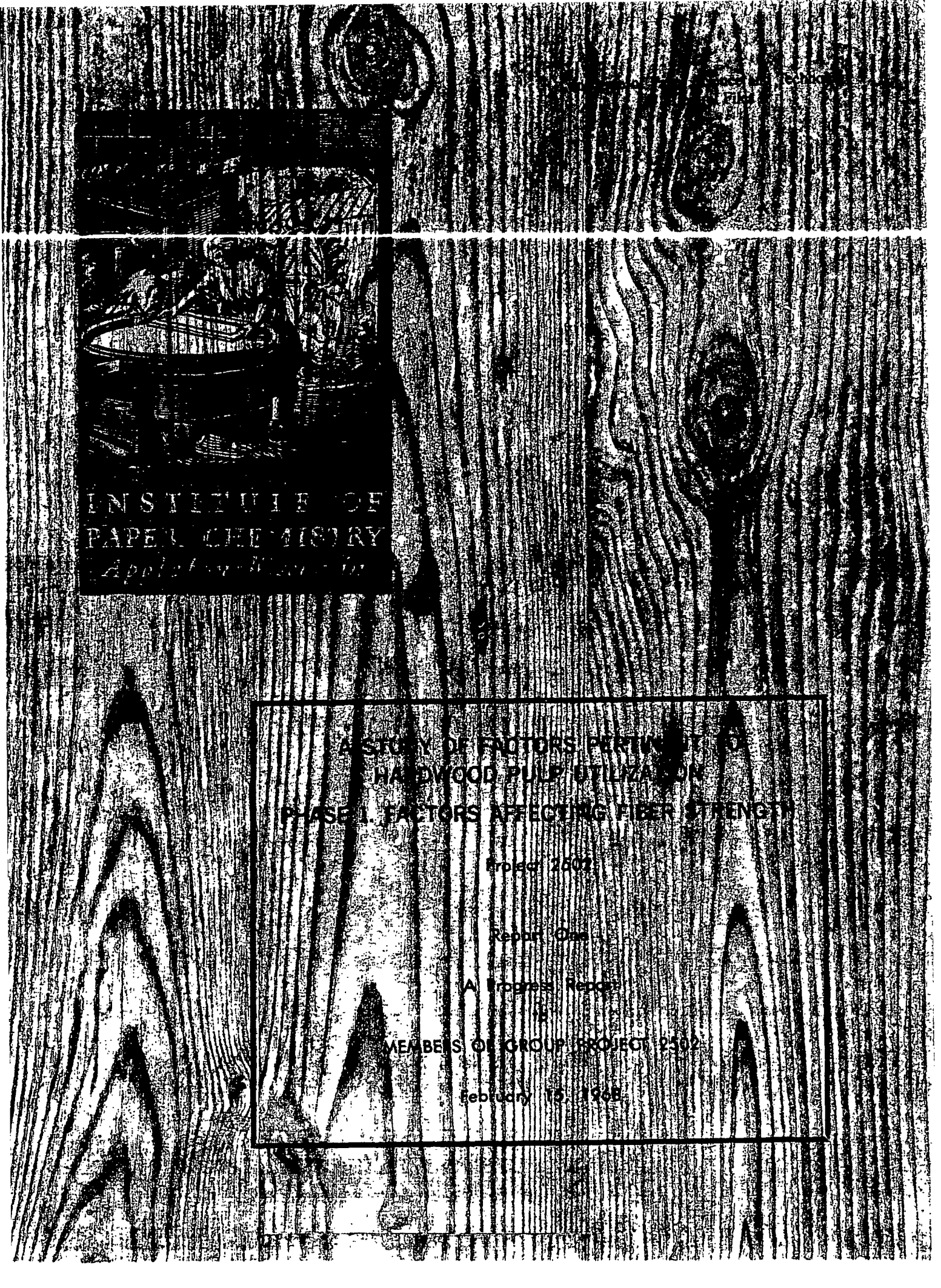

A STUDY OF FACTORS PERTINENT TO HARDWOOD PULP UTILIZATION

PHASE I. FACTORS AFFECTING FIBER STRENGTH

Project 2502

Report One

A Progress Report

by

MEMBERS OF GROUP PROJECT 2502

February 15, 1968

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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Appleton, Wisconsin

A STUDY OF FACTORS PERTINENT TO HARDWOOD PULP UTILIZATION

PHASE 1. FACTORS AFFECTING FIBER STRENGTH

SUMMARY

The original plans for this project included three phases: 1. The effects of fiber structure and chemical properties on fiber strength, 2. The relation of fiber strength, fiber length, and sheet structure to tear and tensile strength of the sheet, and 3. The influence of ray cells and vessel segments on sheet properties. This report concerns only the first phase and only the work with low lignin content pulps.

An aspen kraft pulp, a chlorited aspen pulp and a chlorited oak pulp were subjected to a series of alkali extractions in both aqueous and emulsion form. The resulting pulps were tested for yield, carbohydrate content, viscosity, x-ray diffraction, and zero-span tensile strength. In general, increasing severity of treatment caused decreases in viscosity, xylan content, and strength, with the aqueous treatments being more drastic than the emulsion ones. In specific combinations of wood species, pulping process and aftertreatment, correlations of strength with xylan content and/or with viscosity can be found but these correlations become of less significance when applied to more general situations. Future investigations on the factors controlling fiber strength can now be based on a more complete evaluation of the chemical components of the fiber, the structure of each species of fiber, and the effects of various processing operations. Continuation of the original approach to this phase did not appear to be advisable when these results and concurrent research are considered.

GENERAL BACKGROUND

Economic considerations have dictated an increasing interest in hardwood pulps, and research on better utilization of hardwoods has been carried out in many laboratories. In particular, Group Project 2070, "Strength Properties of Hardwood Pulps" provided a background for further study of several specific aspects. A proposal for continued research was submitted in May, 1964 and a project based on this proposal was initiated as of August 1, 1964, with the sponsorship of 21 companies. In that proposal the evaluation of hardwood pulps was discussed, with particular emphasis on three aspects: fiber properties, process variables, and sheet properties, with various interrelations between them. The studies proposed were aimed at developing relationships between the chemical and mechanical properties of fibers, between fiber properties and process variables, and between fiber properties and sheet properties.

The factors relevant to the evaluation of hardwood pulps were outlined as shown in Fig. 1. Although the diagram provides a qualitative relationship between these factors, quantitative relationships are lacking. One typical deficiency of hardwood pulps is the reduction in tearing strength which usually accompanies their use. Tearing resistance is believed to be influenced by fiber length, fiber strength, and sheet structure but the manner of interaction is not clear. For example, previous work showed that an aspen sheet was lower in tear strength than an oak sheet even though the oak fiber strength was lower than that of the aspen and the average fiber length of the two pulps was essentially the same. Assuming higher tear could be achieved by higher fiber strength, we do not know how much potential fiber strength is possible from a given wood species or how effectively the strength is retained in commercial processing procedures. In order to guide research on improvement of pulping and refining techniques on hardwood fibers, a better knowledge of the relationship

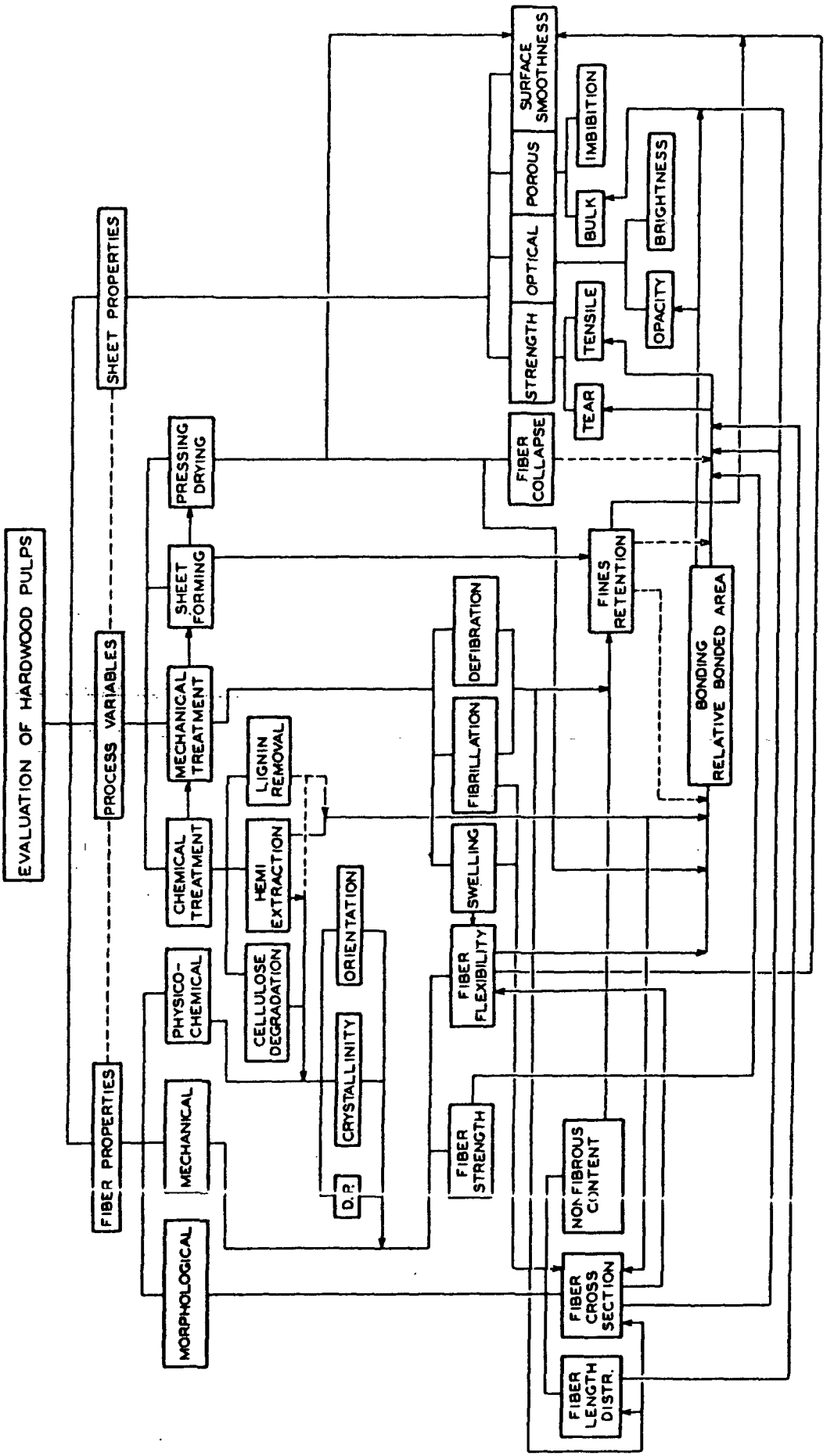

Figure 1. Evaluation of Hardwood Pulps

between the physical/chemical properties of the fibers and their strength properties is required.

Certain problems in the use of hardwood pulps appear to be particularly critical. The reduction in tearing strength which often results from use of hardwood pulps may be due in part to short fibers but is also influenced by the strength of the fibers and the extent of interfiber bonding. In addition, these three factors have a large influence on the sheet tensile strength. Fiber strength and fiber length distribution can be evaluated by available techniques but fiber-fiber bonding and sheet structure in general are complex subjects and difficult to evaluate. Hardwood pulps are also characterized by the presence of large amounts of nonfibrous elements (ray cells and vessel segments) and the contribution of these elements is not fully understood. Sheets containing hardwood fibers are usually characterized by good opacity and bulk, properties which should be retained or increased if possible.

From consideration of these factors a research project was proposed to include the following areas of investigation:

1. The effects of hardwood fiber structure and chemical properties on fiber strength.
2. The relationships between fiber strength, fiber length distribution, and degree of interfiber bonding and the tear and tensile strength of the sheet.
3. The influence of hardwood ray cells and vessel segments on sheet properties.
4. The relationships between hardwood fiber properties and sheet structure on one hand and sheet opacity and bulk on the other.

The proposed program emphasized the first three aspects because of the emphasis placed upon them during the final phases of Group Project 2070. This report is concerned only with the first aspect; subsequent reports will discuss research initiated on the other aspects.

APPROACH

Fiber strength is recognized to be an important and, in some cases, a controlling factor in its influence on the strength properties of sheets. Because of the lower strength usually associated with papers containing hardwood pulps, a better knowledge of possible means for improving strength is particularly pertinent. Although hardwoods do contain more nonfibrous material than softwoods do, they still consist mainly of fibers or tracheids and this phase of the work was directed toward investigating the factors in the fiber structure which influenced the strength of the fiber. In order to avoid the complications of bonding introduced by evaluation of pulps in the form of handsheets, evaluation of fiber strength was approached by means of the improved zero-span tensile test, which has been shown to be a valuable indication of the ultimate strength of the fibers themselves and to be influenced to only a minor extent by factors of bonding and sheet structure. This correlation has been established by comparisons of zero-span tensile strength of handsheets with the strength of individual fibers but zero-span testing is a less time-consuming method of evaluation.

The following factors were suggested as contributing to the ultimate strength of fibers under applied tension:

1. residual lignin content,
2. degree of polymerization (D.P.),
3. hemicellulose composition and content,

4. crystallinity of carbohydrate components, and

5. orientation of carbohydrate components.

The difficulty in studying the relationship of these factors and their influence on fiber strength lies in the difficulty of controlling any one of these factors independently of the others. Thus, lignin is often considered to be a filler and may not in itself contribute much to the strength of the fiber. However, the presence of the lignin, in addition to adding to the fiber mass, may result in a different fiber structure or arrangement of the carbohydrate portion of the fiber, and thereby exert a subtle but no less important effect on the fiber property. In the current work, varying degrees of delignification were planned with minimum carbohydrate degradation by using low temperature chloriting procedures, with the initial work to be done with pulps of comparatively low lignin content.

Correlations between degree of polymerization of cellulose and fiber strength have been found for cotton fibers with the dependence being strongest at average D.P. values below 500. Theories have been advanced to explain this effect in a physically homogeneous fiber, but neither cotton nor wood fibers are structurally homogeneous and many other factors must be included to explain the strength properties. In hardwood fibers especially, the noncellulosic carbohydrate content may make interpretation of this relationship especially difficult.

The hemicellulose content of fibers has often been associated with the development of interfiber bonding and previous work has shown a correlation between hardwood fiber strength and hemicellulose content. However, methods for controlling the hemicellulose removal, such as by alkaline extraction, may involve not only extraction of the hemicelluloses but also drastic changes in the nature of the unextracted material and in the structure of the fiber.

The degree of crystallinity and the orientation of the carbohydrate polymer molecules may also be important. Degree of crystallinity refers to the proportion of the molecules which are included in highly ordered regions; orientation refers to the extent to which these molecules are aligned with respect to the fiber axis. Separation of these two effects is not easy.

The general approach for study of these factors was outlined in the proposal as shown schematically in Fig. 2. Pulps of several degrees of delignification were to be achieved with a minimum of degradation of the carbohydrate by the use of a low-temperature chloriting procedure. By extraction with alkali of several concentrations, varying amounts of hemicelluloses could be removed but with simultaneous changes in fiber structure. For comparison, structural changes in these base-line pulps with minimum degradation and hemicellulose removal were planned by adapting the method described by Centola, Borruso, and Moruzzi (1). This method involves the use of an alkali-water-ligroin emulsion and is claimed to allow for the swelling action of alkali without the usual removal of hemicellulose. The use of low temperatures and short times should minimize any degradation. The use of several alkali concentrations should permit varying amounts of hemicellulose removal and of changes in crystallinity and orientation to permit a study of these effects and their influence on fiber strength. Experiments in the higher temperature range would increase degradation and contribute additional information on the importance of polymer D.P.

Aspen and white oak were selected as the wood species because they represent extreme variations in hardwoods with the oak containing thick-walled stiff fibers and a high percentage of ray cells and the aspen representing a thin-walled, readily collapsible fiber with relatively few ray cells. In addition, a typical commercial

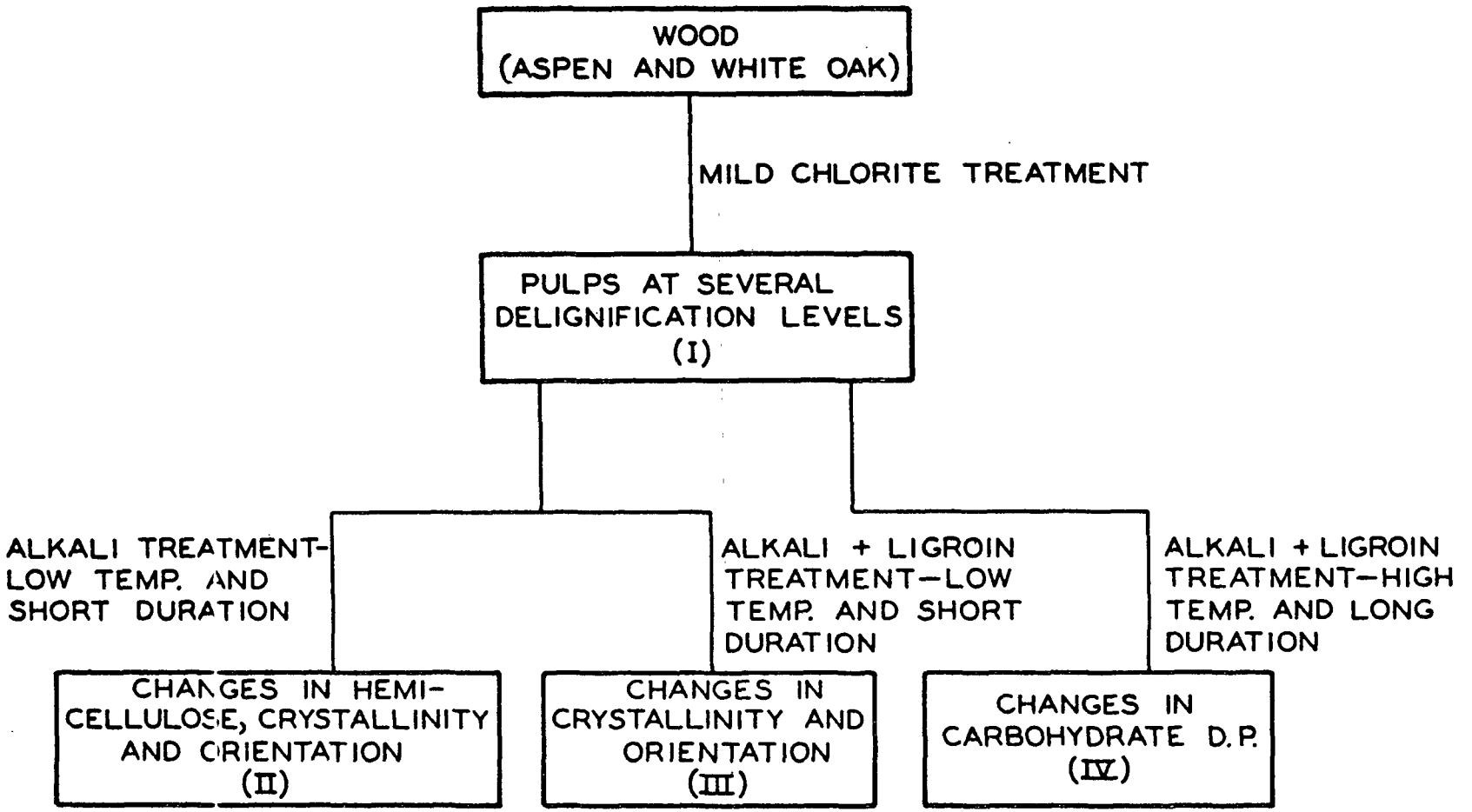

Figure 2. Experimental Approach for Phase 1

hardwood pulp was to be included for comparison to determine whether its strength behavior would be consistent with that expected from those pulps produced by mild chloriting.

EXPERIMENTAL PROCEDURES

PREPARATION OF PULPS

Three different pulps were used, one commercial and two laboratory ones. A five-pound sample of a never-dried commercial bleached aspen kraft pulp was received from one of the sponsors of the project. This pulp had been prepared from aspen, sap-peeled and aged six months before use. Nominal 1/2 to 5/8-inch chips were cooked in batch digesters following conventional cooking conditions with 16% active alkali (as Na_2O) at 25% sulfidity, to yield an unbleached pulp with a permanganate number of 11 and a yield of 51%. The pulp was bleached by a lime chlorination-hypochlorite-peroxide bleaching sequence to a brightness of 86-87%. A bleaching yield of 95% gave an overall yield of 48.5%. This pulp was selected in the hope of having a wood species with morphological characteristics similar to those of the aspen laboratory pulps.

The two laboratory pulps were prepared in the same manner, one from a freshly cut aspen log and one from a freshly cut white oak log. The logs were barked and chipped, and the chips then hand sorted to remove knots and air dried. They were then extracted to remove resinous materials and subjected to chloriting at room temperature according to the modification proposed by Thompson and Kaustinen (2) of the elevated temperature method described by Wise, Murphy, and d'Addieco (3).

The air-dried chips were extracted first with an ethyl alcohol-chloroform mixture (1:1) to remove extractives, then with ethyl alcohol and finally with water.

All of the extraction steps were carried out under a slight vacuum at room temperature. The chips were given a final wash with acetone and air dried. A stock solution of sodium chlorite was prepared in distilled water with a concentration of 100 g./l. The pH was adjusted to 6.8 with glacial acetic acid and the liquor added to the chips. A vacuum was applied for 1/2 hour to aid penetration. The vacuum was removed and the pH readjusted to 4.0. The samples were then reacted at room temperature under 5-inches water pressure.

At the end of each two-day period the chips were washed free of chlorite with water, given a final wash with acetone and air dried. The same procedure of adding the chlorite was repeated until the desired level of delignification had been reached (below 1.0% in this series). Four such treatments were required to obtain a pulp for aspen, while five were needed with the white oak.

The chlorited chips were then given a sodium borohydride reduction at pH 8.0. The main intent of this step was to soften the chips so they could be easily defibrated with minimum mechanical damage and minimum loss of hemicelluloses. The chips were broken up in the Williams stirrer for 5 minutes and screened. The screened pulp was dewatered and stored in the cold room awaiting aftertreatments.

ALKALINE TREATMENTS

Aqueous Alkali

A 40.0 g. (ovendry basis) charge of pulp was slushed in distilled water, drained in a coarse fritted glass Buchner funnel, washed thoroughly with acetone and air dried. Caustic soda solution (943 ml.) at the appropriate concentration (5, 10, 15, and 20% by weight) was charged into a 2-l. resin reaction vessel. Nitrogen was bubbled into the solution to remove the excess air. The solution

was agitated gently (while under nitrogen atmosphere), the pulp added and reacted for one hour at room temperature.

The pulp suspension was filtered, washed thoroughly with water, then with a 5% acetic acid solution and again with water until the pulp slurry was neutral. The pulp was given a final wash in acetone and air dried.

Alkali-Ligroin Emulsion at Low Temperature

The alkali-ligroin extraction is based on a procedure given by Centola, et al. (1) which he found would cause passivation of the cellulose fiber toward beating with comparatively little extraction of hemicellulose.

A 40.0-g. (ovendry) charge of pulp was slushed in distilled water, drained in a coarse fritted glass Buchner funnel, washed thoroughly with acetone and air dried. Eighty-seven ml. of the appropriate concentration (5, 10, 15, and 20% by weight) of a water solution of sodium hydroxide was added to 1885 ml. of ligroin (petroleum ether with a 30 - 60°C. boiling point) and the emulsion mechanically agitated. The pulp sample was added and allowed to react for 3 hours. The slurry was then filtered, washed with 95% ethanol, followed by further washing with a solution of 5% acetic acid in ethyl alcohol, treated with a 5% aqueous solution of acetic acid and washed with water until the slurry was neutral. The sample was given a final wash with acetone and air dried.

No experimental difficulties were encountered in handling the pulps in the aqueous alkali treatments. However, in the alkali-ligroin experiments the fibers formed small pellets which were difficult to defiber and the planned procedure was modified by the addition of 5-minutes disintegration with aqueous 5% acetic acid.

Alkali-Ligroin Emulsion at High Temperature

Pulp samples were prepared for this stage but no plans were made to start these treatments until after establishing that the low-temperature, short-time alkali-ligroin emulsion treatments would yield favorable results.

METHODS OF EVALUATION

Yield

Yields were calculated on an ovendry basis for the pulps and for each aftertreatment of the pulps, and reported both for the treatment and based on the wood.

Degree of Polymerization

An approximate guide to the effect of these treatments on the degree of polymerization of the components of the pulp was obtained by measurement of the viscosity of solutions of pulp in standard cupriethylenediamine (4). This method gives no indication of the distribution of molecular weight of the components of the pulp and it is quite possible that fiber strength will be related more to the molecular weight of specific components than to the average. Techniques are available for determining molecular weight distribution but they are time consuming and any investigation of this aspect was delayed until after the preliminary results were obtained.

Carbohydrate Content

All pulp samples were analyzed for glucan, xylan, mannan, araban, and galactan by standard quantitative paper chromatography of hydrolyzed samples (5). The limit of detection by this technique is 0.5%; detectable amounts of araban or

galactan were not found in any of the samples tested and consequently no results are reported for these two materials. Polyuronides were determined by decarboxylation with 12% HCl and weighing of CO_2 evolved (Institute Method 25).

Zero-Span Tensile Strength

An indication of fiber strength was obtained by the use of the improved zero-span tensile test as described by Wink and Van Eperen (6). Handsheets were prepared in the standard manner except at a basis weight approximately 80% of the standard. The lower basis weight has been found to give a better indication of the true strength of the fibers. The results are reported in pounds per inch width corrected to a 45-lb. basis weight in order to facilitate comparison with the results reported previously under Project 2070. They are also reported in breaking length in meters.

Breaking length may be defined as the length of a strip which would cause a specimen to break under its own weight. It is calculated from the sample width, basis weight, and breaking load and is proportional to the breaking strength in pounds per inch width at a standardized basis weight but avoids the necessity of specifying the basis weight used in the calculations. Breaking length then represents an evaluation of the strength of the material but on a weight basis rather than on a cross-sectional area basis.

In this work there may be interest in comparing the strength of a given number of fibers rather than as a material basis. When a wood is pulped to various degrees the average weight of a fiber will decrease, as indicated by yield; when handsheets are made at a given basis weight (or strength results are calculated to a standard basis weight) the use of a pulp of lower yield will result in including more fibers for a given weight sheet. In order to consider breaking

strength on a constant number of fibers basis, the breaking length was multiplied by the yield to give a figure identified as strength index.

X-ray Diffraction

An estimate of the changes in molecular structure of the samples was obtained by x-ray diffraction measurements. Samples were ground and pressed into pellets for measurement with a Norelco x-ray unit operating with parafocusing geometry. The K-alpha radiation was obtained from a copper target tube operated at 35 kilovolts and 20 milliamperes with a nickel filter. The x-ray was collimated with half-degree divergence and scatter slits and a 0.006-inch receiving slit.

Several techniques were used in analyzing the diffractograms in order to obtain useful indications of changes of structure on a large number of samples without excessive consumption of time. Crystallinity index was calculated as proposed by Segal, Creely, Martin, and Conrad (7), according to the equation

$$\text{Crystallinity index} = \frac{100(I_{002} - I_{am})}{I_{002}}$$

where I_{002} = the intensity of diffraction of 002 plane

I_{am} = the intensity of the amorphous background measured at $2\theta = 18°$

These authors compared this empirical method for estimating crystallinity with other recognized methods on samples of native cellulose (cotton linters) and showed considerable saving of time and good correlation. However, when cellulose II is present, it will influence this index as pointed out by Gillespie, Mueller, Swenson, and Ward (8). In the presence of alkali of sufficient concentration, varying amounts of cellulose II are formed, causing a decrease in the intensity

of the 002-plane diffraction peak at approximately $2\theta = 22.6°$. The base of the peak becomes wider and less well defined as the 10$\bar{1}$-plane diffraction peak of the cellulose II lattice becomes evident at $2\theta = 20.0°$. As an indication of this shift, the width of the 002 peak at half height is shown in the tables for any diffraction measurements where it was considered significant. The width at half height of a peak is inversely proportional to size and/or the amount of imperfection of the crystallite. When cellulose II is present in sufficient quantity, the 002 peak is not resolved well enough to permit obtaining a significant measurement at half height and in these cases the figures are omitted.

The amount of cellulose II present in the sample was estimated by comparing the x-ray diffraction patterns with those published by Ellefsen, Lund, Tonnesen, and Oien (9) for known mixtures of cellulose I and cellulose II.

Orientation

At the time the project was initiated, the potential importance of orientation of the crystallites or macromolecules with respect to the fiber axis was recognized. The techniques available were time-consuming and involved measurements on single fibers, such as by x-ray analysis. Other techniques were being considered in academic research but did not prove to be feasible and no measurements of orientation were made.

RESULTS AND DISCUSSION

BASE PULPS

The yields and characteristics of the three base pulps are shown in Table I. It will be noted from the results on carbohydrate content that the tests used totalled slightly over 100% for the commercial kraft pulp (probably within limits of the test), slightly less than 100% for the laboratory aspen, and significantly less for the laboratory oak pulp. The following analysis for trembling aspenwood is taken from Timell (10):

Glucan	57.3
Mannan	2.3
Galactan	0.8
Xylan	16.0
Araban	0.4
Uronic anhydride	3.3
Acetyl	3.4
Lignin	16.3
Ash	0.2

Allowing for limits of the test and the presence of small amounts of araban, galactan, and ash, the principal missing components of the pulps probably are acetyl and a modified form of lignin. Browning and Bublitz (11) showed the presence of significant amounts of acid-soluble lignin in spruce holocellulose prepared by acidified chlorite treatment. White oak is reported with lignin contents much higher than aspen, and the presence of higher percentages of modified lignin in the oak pulp seems probable. A further source of error may lie in the failure of the sugar hydrolysis method to show all xylan when uronic acids are present.

TABLE I

CHARACTERISTICS OF BASE PULPS

Species	Aspen		White Oak
Pulp	Kraft	Chlorited	Chlorited
Yield, %	48.5	65.5	59.7
Zero-span strength			
Breaking load, lb./in.	42.5	57.0	46.2
Breaking length, meters	12,000	16,100	13,000
Strength index[a]	5,820	10,520	7,760
Carbohydrate content[b]			
Glucan, %	80.7	67.0	59.6
Xylan, %	22.9	20.9	21.1
Mannan, %	< 0.5	2.3	1.3
Polyuronides, %	0.3	4.4	3.8
Total, %	103.9	94.6	85.8
Structure			
Viscosity, cp.	6.24	11.8	12.3
Crystallinity index	77.4	59.8	45.8
Width of 002 peak, degrees 2θ	2.0	2.9	3.4
Conversion to cellulose II, %	0.0	0.0	0.0

[a] Product of breaking length and yield.

[b] Less than 0.5% araban and 0.5% galactan in all cases.

In accordance with previous experience, the chlorited aspen pulp was stronger than the chlorited oak pulp and also stronger than the aspen kraft. Although the laboratory pulps were prepared by a procedure expected to be mild, the viscosities of these pulps were rather low. According to the Hercules conversion chart (12), viscosities of 6.2, 11.8, and 12.3 correspond to D.P.'s of approximately 800, 1080, and 1100.

It may be of interest to compare these results with those obtained in Project 2070 in two separate phases of that program. In the earlier part (Reports 5 and 6) pulps were prepared by high temperature chloriting of neutral sulfite semichemical pulps. Later in that project, pulps were prepared by room temperature chlorite treatment of aspenwood in a manner similar (but not identical) to that used in the current project. The conditions of preparation and some characteristics of the pulps are compared in Table II. In both cases where wood was chlorited, the wood was extracted first with chloroform and alcohol; in the current project, this was followed by rinses with alcohol, water, and acetone before allowing the chips to air dry. In the current project, chlorite treatments were handled in two-day steps in order to monitor the delignification. As a result, the chips were probably handled more, introducing greater mechanical losses. In addition, the current pulps were given a borohydride treatment at pH 8 which was not used on the previous pulps.

Viscosities of all pulps prepared by room-temperature chloriting were considerably lower than those obtained by high-temperature chloriting of the pulps previously cooked by a neutral sulfite semichemical process. Zero-span tensile strength in both cases was significantly lower, suggesting that the low-temperature chloriting procedures are not necessarily mild with respect to degradation. In the current work, this chloriting procedure, including the extra handling and

TABLE II

THE EFFECT OF VARIOUS METHODS OF PREPARATION OF PULPS

Project	2070-early	2070-late	2502
Reference	Report 6	Report 11	Report 1
Preparation			
Raw material	NSSC pulp	Wood	Wood
Chlorite concn., g/l.	100	150	100
Temperature, °C.	75	Room	Room
Time of treatment, hr.	4	168	192[a]
Aspen – Yield, % on wood	62	79	65.5
– Viscosity, cp.	43	14	12
– Zero-span strength, lb./in.	66	64	57
– Solubility in 10% NaOH, %[b]	20	-	32.0
Oak – Yield, % on wood	60	76	59.7
– Viscosity, cp.	34	12	12
– Zero-span, lb./in.	58	50	46

[a] 240 Hours for the oak pulp.

[b] Result for 2070-early by TAPPI T-235; that for 2502 from yield of extraction reported below.

borohydride reduction, resulted in a yield considerably lower than that for a pulp of comparable viscosity obtained earlier, suggesting possibility of mechanical losses.

The alkali solubilities were not run under comparable conditions but furnish further basis for speculation. The higher alkali solubility of the pulp chlorited at room temperature could show either greater degradation of the material left in the pulp or a pulp which retained more of the original alkali-soluble material from the wood. The latter possibility implies either a greater removal by high-temperature chloriting of nonalkali-soluble components or again that we consider the yield of 2502 pulp to be too low.

THE EFFECT OF TREATMENTS ON CHEMICAL PROPERTIES

The objective in this phase of the program was to investigate further the relative influence of xylan or other hemicelluloses and structure on fiber strength; in order to obtain various combinations of effects two techniques were used at several concentrations, one being conventional aqueous alkali extraction and the other the alkali-ligroin emulsion proposed by Centola, et al. (1). The results are tabulated in Table III for the aspen kraft, Table IV for the chlorited aspen, and Table V for the chlorited oak pulp.

Before attempting to relate xylan content or other characteristics to strength it may be helpful to examine whether or not the expected effects were obtained from these different kinds of treatments. Figure 3 shows the yield versus treatment for the aspen kraft, Fig. 4 for the chlorited aspen, and Fig. 5 for the chlorited oak pulp. As would be expected from the method of preparation, the aspen kraft was more resistant to all kinds of alkaline extraction than was the chlorited pulp, which had not previously been exposed to any alkaline conditions.

TABLE III

THE EFFECT OF TREATMENTS ON COMMERCIAL ASPEN PULP

Treatment	None	Aqueous Alkali				Alkali-Ligroin			
Concentration	-	5	10	15	20	5	10	15	20
Yield, %									
In treatment	-	88.9	83.0	84.2	82.8	97.4	97.0	99.5	100.0
On wood basis	48.5	43.1	40.3	40.8	40.2	47.2	47.0	48.3	48.5
Zero-span strength									
Breaking load, lb/in.	42.5	38.8	31.6	32.9	36.0	35.0	31.4	28.9	29.4
Breaking length, meters	12,000	11,000	8,930	9,290	10,200	9,870	8,850	8,170	8,310
Strength index[a]	5,820	4,700	3,600	3,800	4,100	4,650	4,150	3,940	4,030
Carbohydrate content[b]									
Glucan, %	80.7	92.3	92.7	94.9	96.1	83.4	82.6	81.5	80.2
Xylan, %	22.9	9.2	4.7	4.3	4.4	18.9	18.3	18.0	18.5
Mannan, %	<0.5	<0.5	<0.5	<0.5	<0.5	0.5	0.7	0.7	0.6
Polyuronide, %	0.3	0.2	0.3	0.4	0.3	0.6	0.6	1.0	1.2
Total, %	103.9	101.7	97.7	99.6	100.8	103.4	102.2	101.2	100.5
Structure									
Viscosity, cp.	6.24	5.47	4.48	4.71	4.94	5.48	4.98	4.13	3.66
Crystallinity index	77.4	71.2	58.8	50.3	56.5	70.5	60.8	44.4	43.7
Width of 002 peak, degrees 2 θ	2.0	2.0	-	-	-	2.1	-	-	-
Conversion to cellulose II, %	0.0	20.0	50.0	80.0	90.0	10.0	30.0	40.0	80.0

[a] Product of breaking length and yield.

[b] Less than 0.5% araban and 0.5% galactan in all cases.

TABLE IV

THE EFFECT OF TREATMENTS ON CHLORITED ASPEN

Treatment	None	Aqueous Alkali				Alkali-Ligroin			
Concentration	-	5	10	15	20	5	10	15	20
Yield, %									
In treatment	-	72.0	67.6	67.3	66.9	85.0	83.5	82.2	81.8
On wood basis	65.5	47.2	44.3	44.1	43.8	55.7	54.7	53.8	53.6
Zero-span strength									
Breaking load, lb./in.	57.0	37.7	35.1	34.8	30.6	45.2	38.4	32.7	33.0
Breaking length, meters	16,100	10,600	9,910	9,830	8,640	12,800	10,800	9,230	9,300
Strength index[a]	10,500	5,000	4,400	4,300	3,800	7,100	5,900	4,900	5,000
Carbohydrate content[b]									
Glucan, %	67.0	85.4	89.3	88.0	92.1	77.5	75.4	75.6	77.9
Xylan, %	20.9	5.0	1.4	1.6	1.6	17.5	12.2	11.2	12.6
Mannan, %	2.3	3.1	1.5	0.9	0.8	2.8	2.7	2.6	2.7
Polyuronide, %	4.4	2.0	1.4	1.5	1.3	3.7	3.2	3.6	3.4
Total, %	94.6	95.5	93.6	92.0	95.8	101.5	93.5	93.0	96.6
Structure									
Viscosity, cp.	11.80	8.44	3.40	3.27	3.53	8.86	6.68	5.56	4.70
Crystallinity index	59.8	64.5	53.0	49.3	50.0	60.5	58.4	52.7	46.5
Width of 002 peak, degrees 2θ	2.9	2.5	-	-	-	2.9	2.9	-	-
Conversion to cellulose II, %	0	10.0	40.0	90.0	100.0	10.0	20.0	30.0	40.0

[a] Product of breaking length and yield.

[b] Less than 0.5% araban and 0.5% galactan in all cases.

TABLE V

THE EFFECT OF TREATMENTS ON CHLORITED WHITE OAK PULP

Treatment	None	Aqueous Alkali				Alkali-Ligroin			
Concentration	-	5	10	15	20	5	10	15	20
Yield, %									
In treatment	-	68.0	67.1	65.6	64.6	82.0	80.5	79.5	79.5
On wood basis	59.7	40.6	40.1	39.2	38.6	49.0	48.1	47.5	47.5
Zero-span strength									
Breaking load, lb./in.	46.2	37.3	30.7	32.1	35.6	39.2	37.9	33.0	30.9
Breaking length, meters	13,000	10,500	8,660	9,050	10,100	11,100	10,700	9,300	8,720
Strength index[a]	7,800	4,300	3,500	3,600	3,900	5,400	5,100	4,400	4,100
Carbohydrate content[b]									
Glucan, %	59.6	83.1	85.3	84.1	84.9	74.1	71.4	71.0	70.1
Xylan, %	21.1	7.4	4.2	5.3	6.9	20.9	19.5	22.5	22.2
Mannan, %	1.3	1.9	3.0	3.5	2.8	3.5	3.5	3.1	3.2
Polyuronide, %	3.8	1.3	1.1	1.6	2.5	2.1	2.4	2.2	2.9
Total, %	85.8	93.7	93.6	94.5	97.1	100.6	96.8	98.8	98.4
Structure									
Viscosity, cp.	12.32	9.54	5.42	4.26	4.03	9.42	7.72	5.66	4.78
Crystallinity index	45.8	60.0	53.3	43.5	39.7	55.2	50.7	44.6	43.7
Width of 002 peak, degrees 2θ	3.4	3.0	-	-	-	3.2	3.4	-	-
Conversion to cellulose II, %	0.0	10.0	40.0	60.0	70.0	10.0	20.0	40.0	50.0

[a] Product of breaking length and yield.

[b] Less than 0.5% araban and 0.5% galactan in all cases.

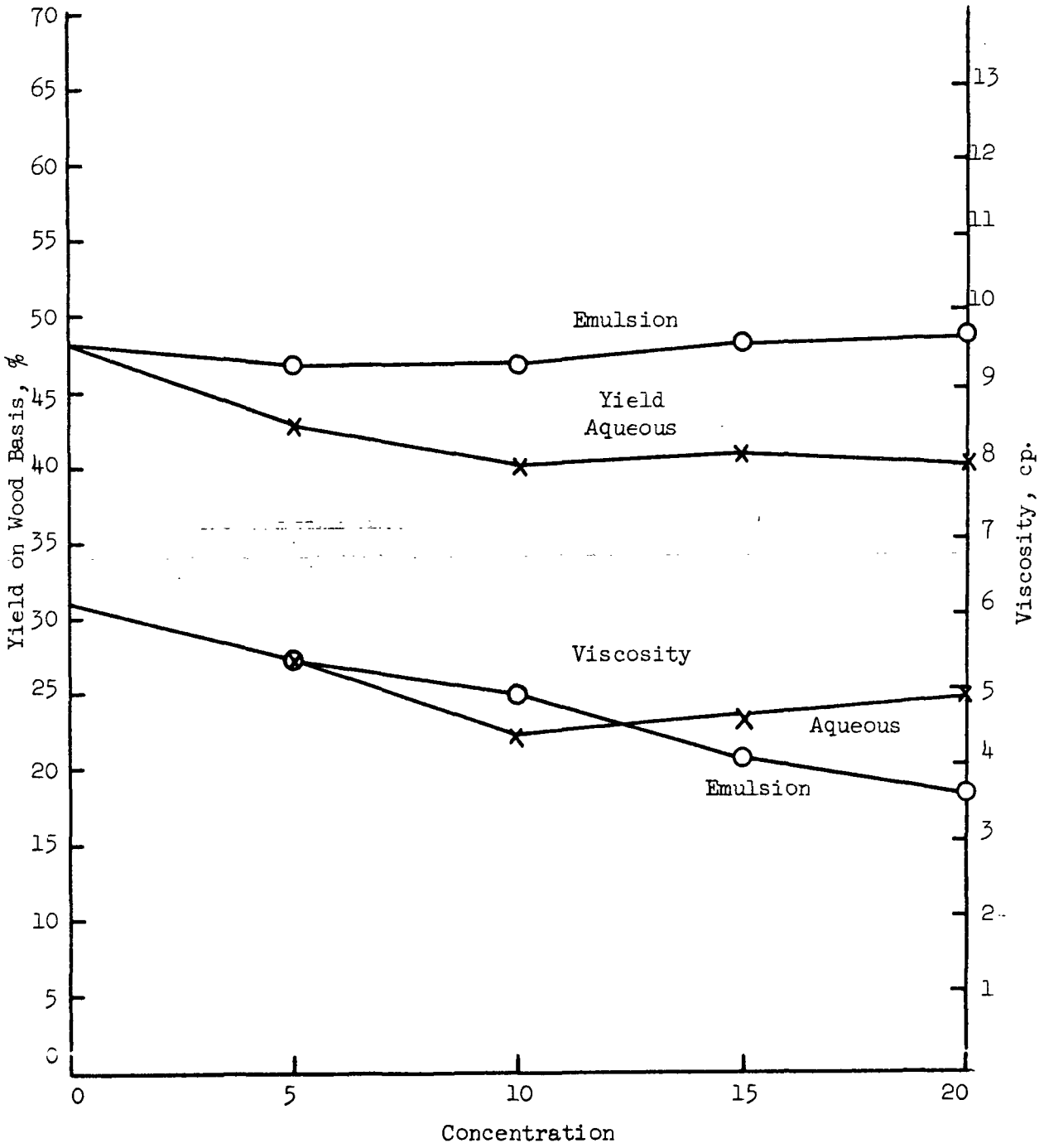

Figure 3. The Effect of Extraction of Aspen Kraft Pulp on Yield and on Viscosity

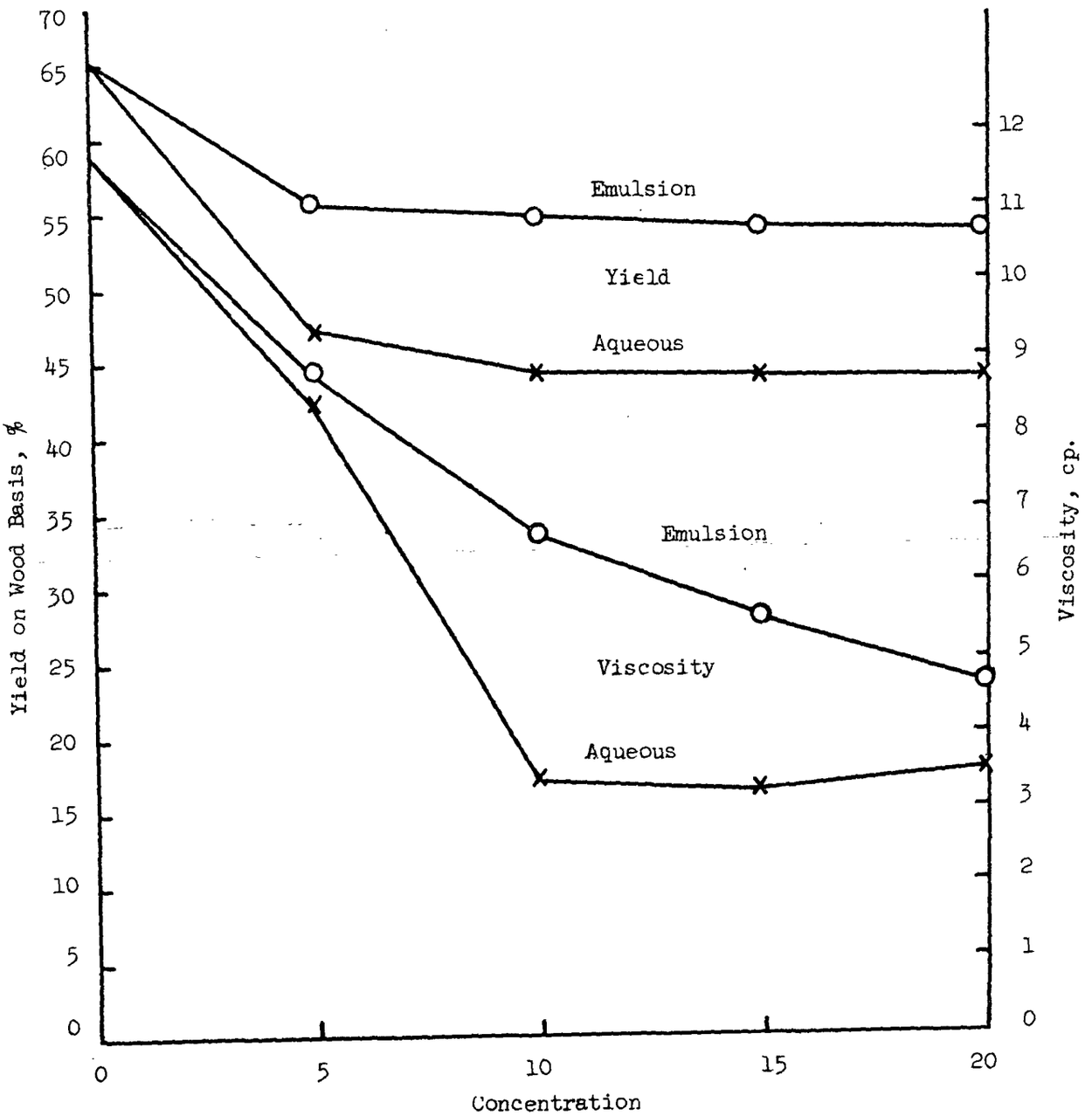

Figure 4. The Effect of Extraction of Chlorited Aspen Pulp on Yield and on Viscosity

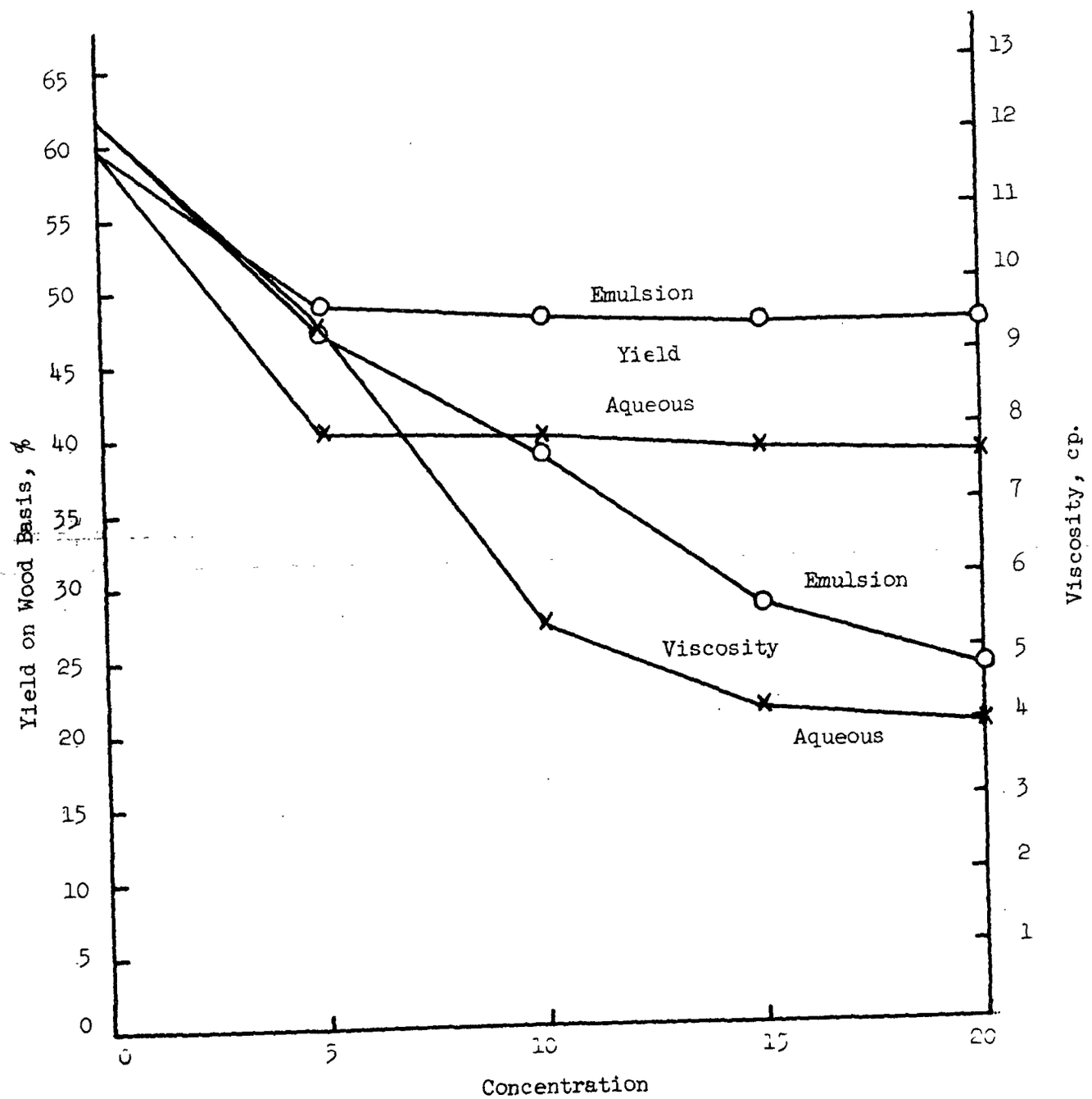

Figure 5. The Effect of Extraction of Chlorited Oak Pulp on Yield and on Viscosity

A part of the difference in quantity extracted may be due to acetyl content and modified lignin which probably were removed in the kraft pulping operation. The emulsion treatment on the aspen kraft removed very little material but the emulsion treatment on the other two pulps did show a significant loss of yield. As expected, because of the greater amount of alkali and water available the aqueous alkali extractions proved to be more drastic in all cases. However, as judged by conversion to cellulose II the alkali available in the emulsion system apparently was adequate to effect a considerable amount of mercerization.

Some interesting effects on viscosity are also shown in Fig. 3-5. Viscosity drops on all treatments but there are interesting differences between the aqueous versus emulsion treatments and the various concentrations. In no case does the viscosity increase over that of the base pulp, as had been reported previously. In the aqueous treatments for the aspen kraft and for the chlorited aspen, there is a slight increase in viscosity of the 20% treatment over that of the 10 or 15% treatments. With the exception of the aspen kraft, the emulsion is less severe in its effect on viscosity than is the aqueous extraction.

A different pattern of removal of hemicelluloses is also apparent. See Fig. 6-8. Cooked to a lower yield, the aspen kraft retained somewhat less of the original xylan in the wood, but had a somewhat higher percentage of xylan in the pulp than the chlorited aspen pulp. On subsequent extraction with aqueous alkali, as well as in the emulsion treatments, the aspen kraft was able to retain a larger proportion of xylan than could be retained in the chlorited aspen pulp at comparable extraction conditions.

Xylan content on both of the laboratory pulps tends to be somewhat higher after the 20% extraction than after the 10% extraction by either aqueous or emulsion method. This effect has been reported previously and may be due either to a "swelling

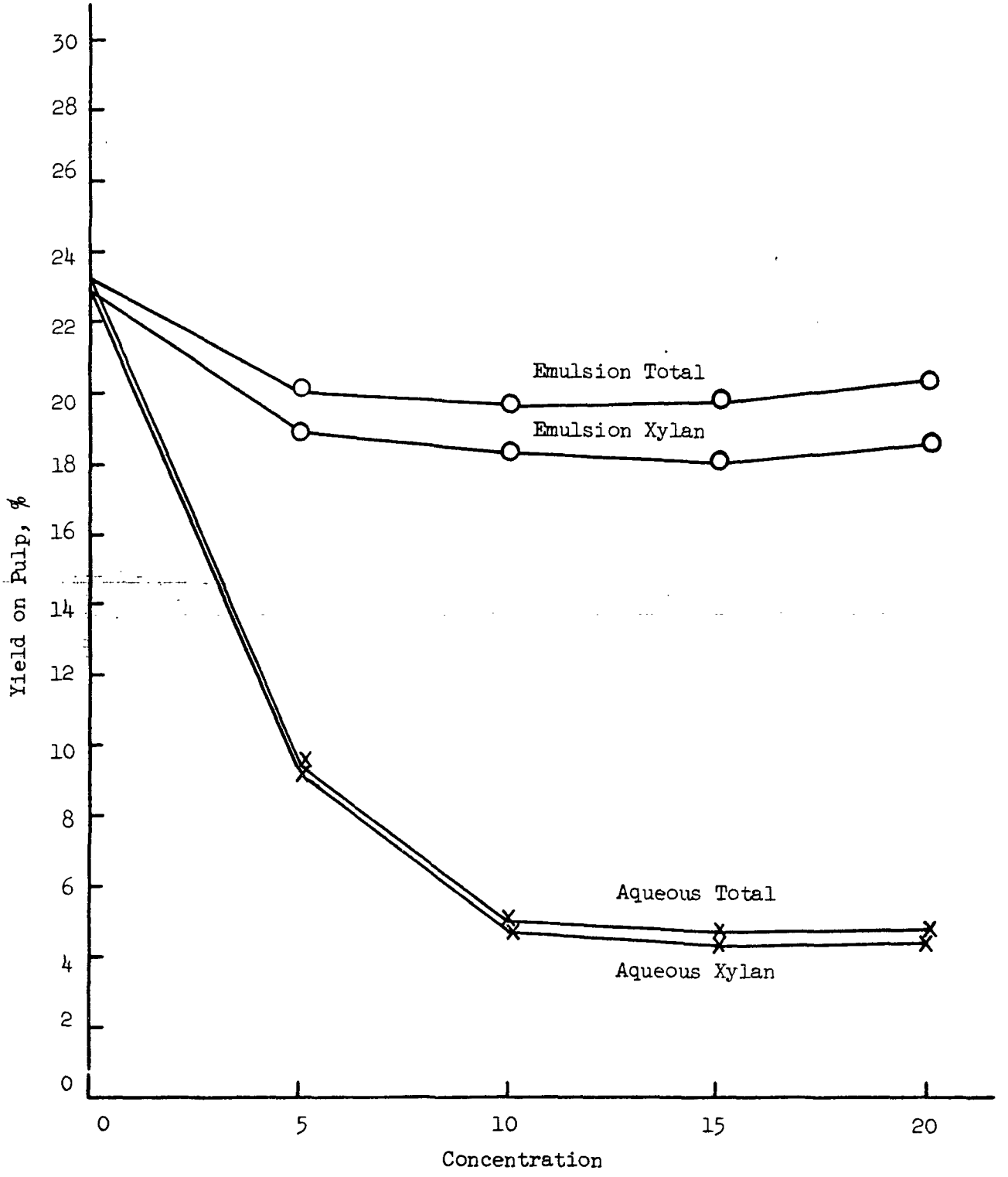

Figure 6. The Effect of Extraction of Aspen Kraft Pulp on Xylan and on Hemicellulose Content

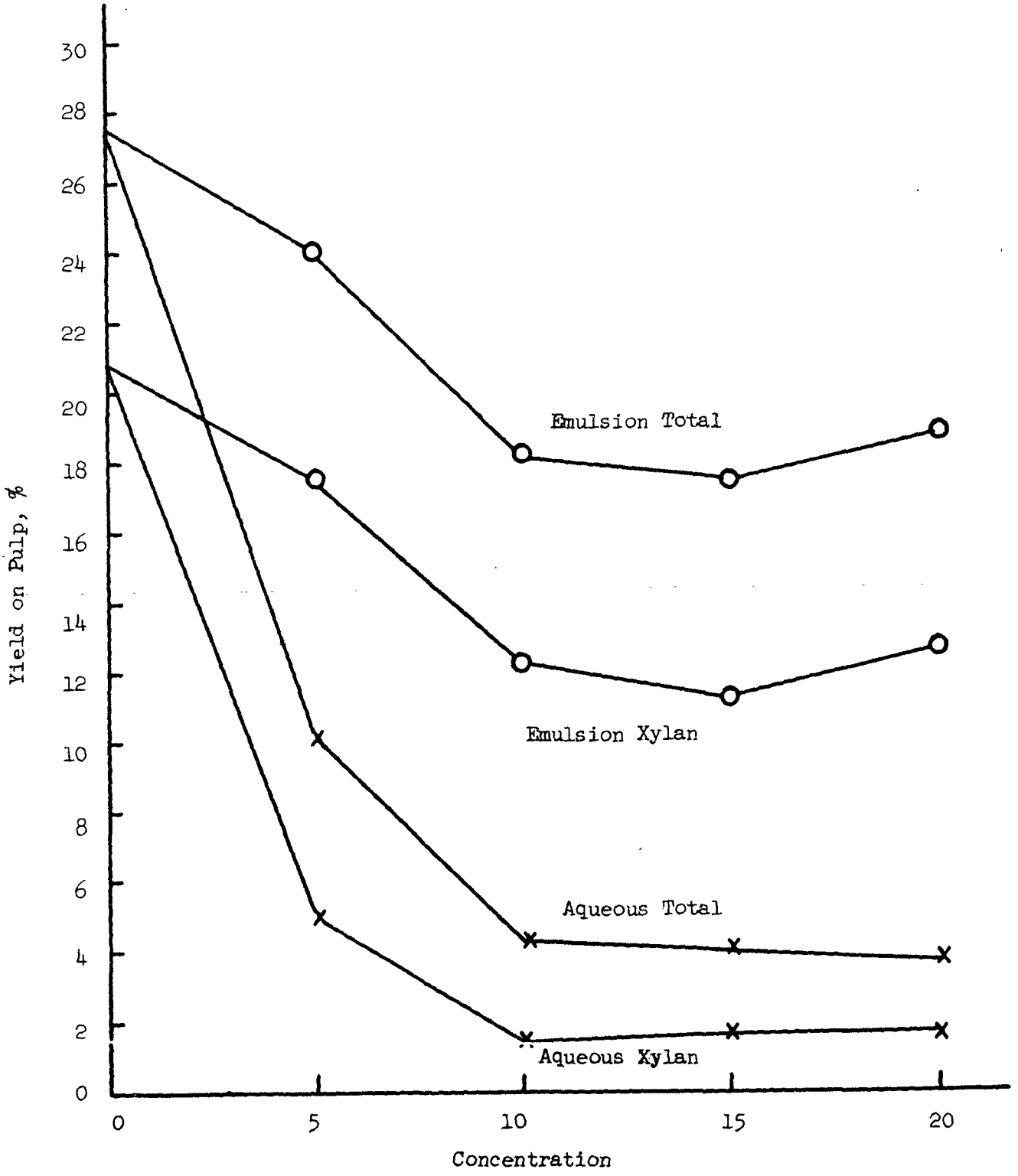

Figure 7. The Effect of Extraction of Chlorited Aspen Pulp on Xylan and on Hemicellulose Content

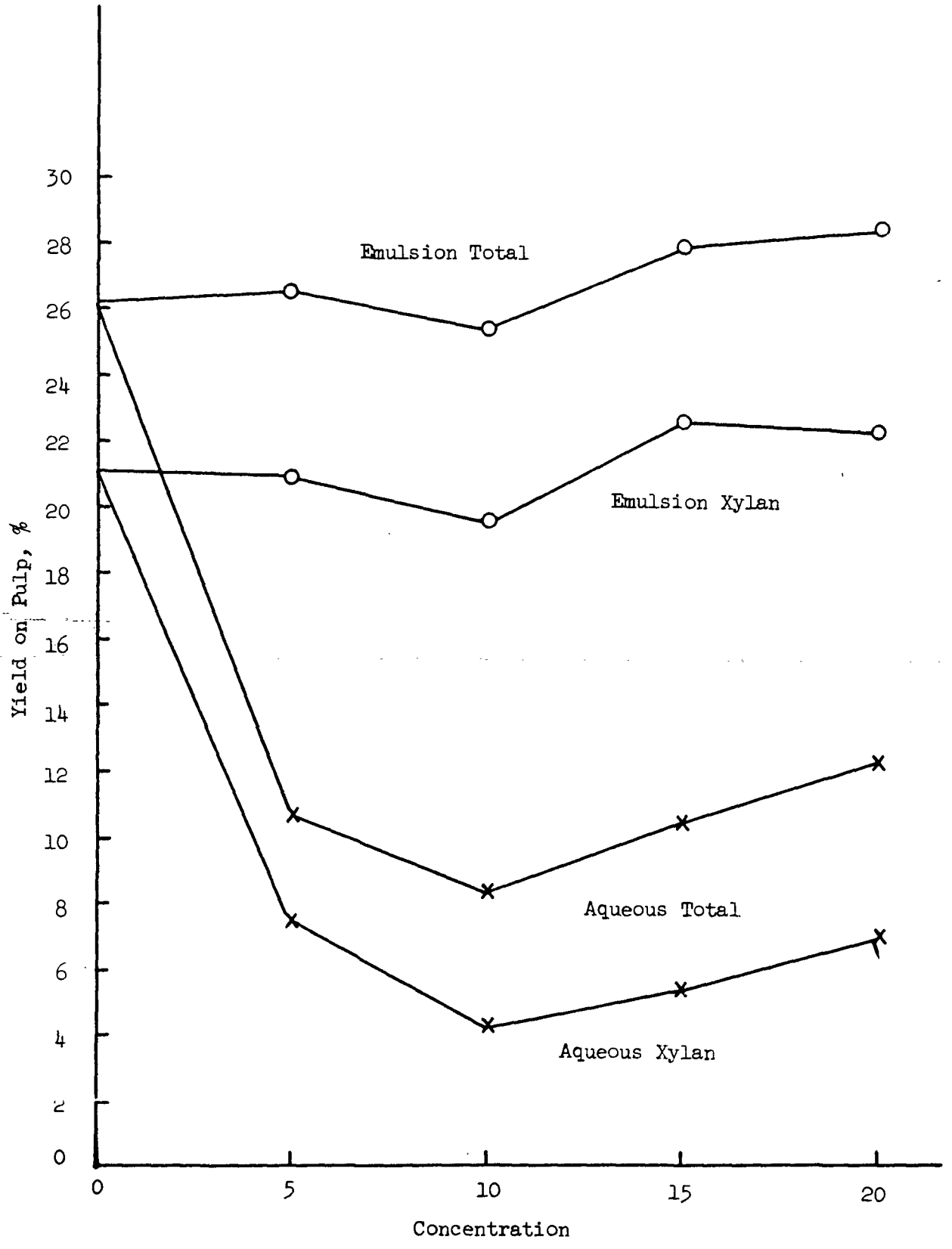

Figure 8. The Effect of Extraction of Chlorited Oak Pulp on Xylan and on Hemicellulose Content

shut" of the fiber structure of the more concentrated alkali or by a salting-out effect. Mannan was almost completely removed in the cooking of the kraft pulp, but an appreciable amount remained in the laboratory-prepared aspen pulp, and a significant amount of this was retained through the alkaline extractions. It is not known whether the apparent formation of mannan by extraction of the chlorited oak pulp with aqueous alkali or by the emulsion system is real or simply experimental error. Polyuronides were low in the aspen kraft base pulp in comparison to the chlorited aspen base pulp, or in this pulp after even the most drastic laboratory extractions.

In considering the x-ray diffraction data, we find that the emulsion approach resulted in less conversion to cellulose II than did the corresponding concentration of the aqueous alkali. Because of the change from cellulose I to cellulose II, the significance of crystallinity index is limited in most cases to the comparison of the 5% treatment with the base pulp. In the commercial aspen kraft, the 5% treatment showed a decrease in crystallinity index with slight or no change in the width at half height of the 002 peak. On the chlorited aspen, the 5% aqueous treatment resulted in an increase in crystallinity and a corresponding increase in the width of the 002 peak. The removal of hemicelluloses could cause an increase in crystallinity index through the removal of the amorphous material, but this would not be expected to cause a change in half-height width which was observed. Katz (13) found that the presence of O-acetyl in a glucomannan prevented molecular orientation, and the presence of acetyl groups in the base pulps may be causing a similar effect here. This change was not obtained in the 5% emulsion treatment of the chlorited aspen pulp. Likewise, Marchessault, Settineri, and Winter (14) found that mild deacetylation applied to white birch holocellulose fibers resulted in crystallization of xylan inside the fiber. Although significant quantities of xylan are left in the fiber by the emulsion treatments, the emulsion approach may not permit crystallization of this material.

On the oak pulp, the original material had a low degree of crystallinity which was increased markedly by the 5% treatment in either aqueous or emulsion form, but most significantly in the aqueous form. Here the width at half-height was also decreased, indicating not only the removal of amorphous material but actually an increase in the crystallinity of the cellulose material itself. The x-ray diffraction pattern of the base pulp made from oak did not have sharp peaks and suggests a distorted cellulose I crystal lattice but the reason is not apparent. The differences in size and degree of perfection of the crystal lattice could be caused by various factors, including different distribution of hemicelluloses.

In summary, we find that, as expected, the aqueous treatments were more severe than the emulsion treatments, although there did appear to be sufficient alkali available in the emulsion treatments to cause significant mercerization. The latter approach was expected to minimize removal of hemicelluloses and it did decrease the removal markedly; there was a decrease of xylan and of total hemicellulose content in both of the aspen pulps, but not in the oak pulp. There was degradation in all cases, with the degradation occurring in the emulsion treatment of the two chlorited pulps being somewhat less severe than that occurring in the aqueous systems.

FACTORS AFFECTING STRENGTH

Figures 9 through 11 show the effect of the treatments on the zero-span tensile strength expressed in breaking length in meters. This is proportional to zero-span strength in pounds per inch width for a standard weight sheet, or, expressed another way, is an evaluation of the strength of the material on an equal weight per unit length of fiber basis. As the weight of a fiber is decreased by extraction, the number of fibers which will enter into a material evaluation of this type increases; therefore, a measure proportional to the strength per fiber may be

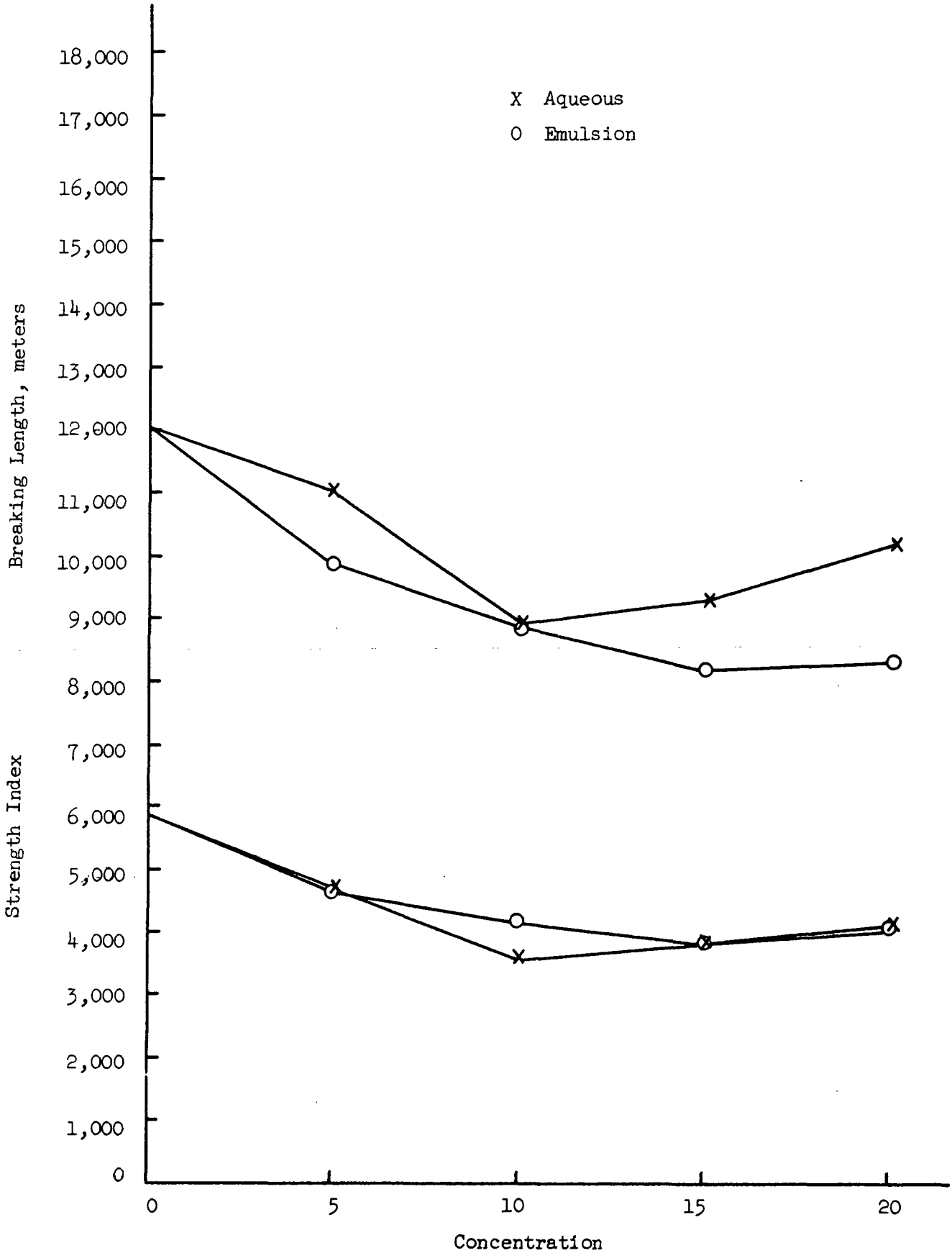

Figure 9. The Effect of Extraction of Aspen Kraft Pulp on Zero-Span Tensile Strength and on Strength Index

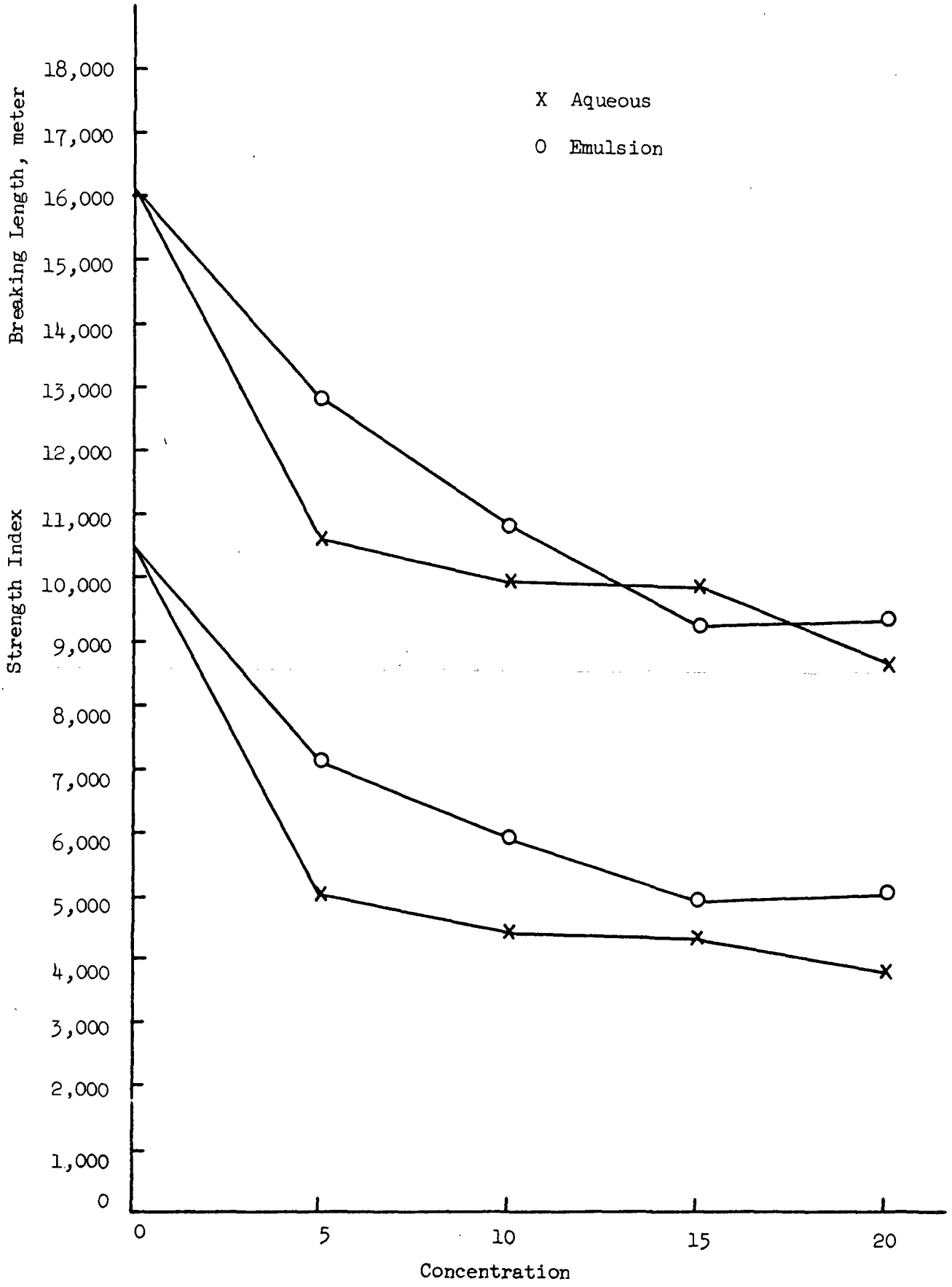

Figure 10. The Effect of Extraction of Chlorited Aspen Pulp on Zero-Span Tensile Strength and on Strength Index

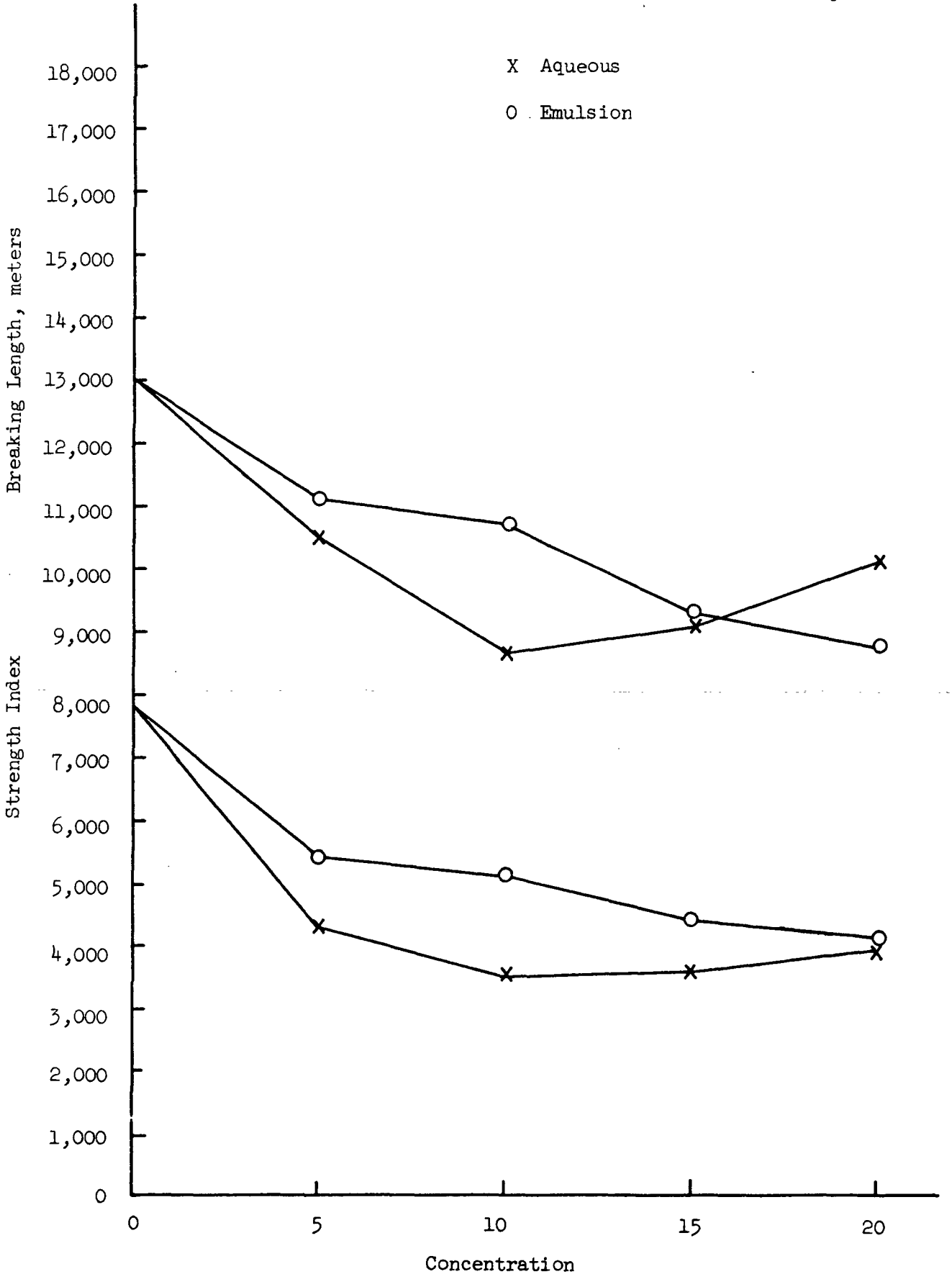

Figure 11. The Effect of Extraction of Chlorited Oak Pulp on Zero-Span Tensile Strength and on Strength Index

obtained by multiplying the breaking length in meters by the yield to give a factor which has been called "strength index."

Again we find that all treatments have decreased both the breaking length and the strength index below the corresponding figure for the base pulp. In some cases, the breaking length reached a minimum at a 10% treatment and then increased at 15 and 20%, but in no case did it reach the original value. In the aspen kraft, the emulsion treatment seemed more severe in its effect on strength than the aqueous treatment, but very comparable when expressed as strength index. On the two chlorited pulps, the emulsion treatment was less severe and the use of strength index seems to give more logical results than breaking length.

When we attempt to relate strength to other causative factors, we find that, in general, strength, xylan content (and total hemicelluloses), and viscosity all decreased with increased severity of treatment; thus, strength may be considered to correlate roughly with both xylan and viscosity. In the less drastic treatments, xylan content and strength appear to correlate in any specific pulp and treatment combination; however, the loss of xylan by aqueous treatment is much more severe than the loss by emulsion treatment, although the changes in strength are more nearly similar. Strength may correlate with xylan in either treatment but does not show the same general correlation for both treatments.

At higher concentrations, the xylan content tends to level off on aqueous treatment of both aspen pulps. On the kraft, a slight increase in viscosity, at 20% might be related to an increase in strength under these conditions. On the chlorited pulp – on the other hand – the xylan, viscosity, and strength all remain constant in going from 10 to 15% concentration aqueous treatment, but then the strength drops sharply with a constant xylan content and a slight increase in viscosity. The

effect is less pronounced on strength index. The analyses show very little difference in the effect of the 15 and 20% treatments except, possibly, for an increase in glucan content. If this difference is significant, there must have been other changes taking place which are not identified completely by the analyses used. In the emulsion treatments at higher concentration, a constant xylan content on the aspen kraft accompanies a decrease in viscosity and a small decrease in strength. On the chlorited aspen, viscosity decreases from 10 to 15 to 20% treatment accompanied by a decrease of both xylan and strength on going from 10 to 15%, and an increase in xylan at 20% with the strength remaining approximately constant.

With the oak pulp, in aqueous treatment the strength and the xylan content follow similar patterns as the viscosity continues to decrease. In the emulsion system, however, the xylan content remains constant or even increases while the strength decreases accompanied by a decrease in viscosity.

It is tempting to exaggerate correlations in specific instances. If we plot strength versus viscosity on the aspen kraft, in the aqueous treatments, we find a fairly good relation to breaking length and a straight-line relation of viscosity to strength index. In the emulsion treatments, the correlation of strength index to viscosity is good for 5 and 10% but deviates at 15 and 20%. Breaking length (or strength index) correlates fairly well with xylan content in the emulsion treatment of this pulp but much less so on the aqueous treatments. On the two chlorited pulps, the situation is reversed, with xylan showing the better correlation in both cases on the aqueous treatment, and viscosity showing the better correlation on the emulsion treatments.

These correlations break down even further when we attempt to include different pulps in the same population of data. Thus, we return to the familiar

situation of finding limited correlations in specific situations but no good generalized correlation, indicating that there are still a number of factors which are not adequately understood. Without doubt, both xylan (or other hemicelluloses) and viscosity are important – at least at certain levels. No unique correlation of fiber strength with any other single property could be demonstrated and probably none should be expected. It is known that viscosity will be important below some critical level and it is quite possible that the viscosities of all the pulps involved are in the critical range. Viscosity, however, is an average value and a better understanding of the distribution of the degrees of polymerization of the various components of the fiber would be more helpful. Xylan content is obviously of importance but it may be more of an indicator of changes taking place in the structure of the fiber than in the chemical content as such. Thus, treatment with alkali in the emulsion form may bring about some of these same changes or may remove some xylan in critical areas without really bringing about the same quantitative removal of xylan.

Working with southern pine fibers, Leopold and McIntosh (15) separated individual fibers by peracetic acid-sodium borohydride treatments and then successive alkaline extractions and found a linear relation between fiber strength and percent of xylan retained but no correlation with mannan content. As a possible explanation, they suggested that the xylan formed the bonding between fibrils and that removal of this bonding weakened the fiber. In subsequent work, McIntosh (16) prepared individual fibers by peracetic acid-borohydride treatment of pine previously cooked by the kraft process to various yields and found no relationship of strength to xylan content but a possible relationship to mannan, to degree of polymerization, and to yield.

The current work utilized the zero-span tensile strength as an indication of fiber strength. Jentzen (17) studied the strength of fibers dried under various degrees of tension and found increases in strength up to 30% or more by drying these fibers under load. He did not study hemicellulose content and found no change in crystallinity by drying under load; he did find a change in the orientation of the fibers, using x-ray diffraction techniques on individual fibers. In the current work, the zero-span tensile measurements were made on sheets dried under restraint and therefore some degree of load was exerted upon the fibers by the tendency to shrink. However, we have no information on the effect of the various treatments upon the shrinkage that would have taken place in these same handsheets dried in an unrestrained condition and, therefore, have no information on the load which may have been exerted upon these fibers by the restraint of the normal process of drying. Centola, et al. (1) discussed the "passivation" of pulp with respect to beating, brought about by alkaline extraction. By analogy, we might expect that alkaline extraction would cause these pulps to show less shrinkage on drying and, therefore, to be dried under less load; in turn, this would cause a decrease in strength as measured by zero-span tensile strength but we have no estimate of the magnitude of this effect.

Spiegelberg (18) made alkaline extracts of pine holocellulose fibers and dried these fibers under load, following Jentzen's technique. He felt that he was able to extract the hemicelluloses without degradation and without mercerization, and found that decreasing hemicellulose content caused an increase in crystallinity and a decrease in strength. He explained these results by considering the hemicelluloses as plasticizers which permitted the fibers to distribute stresses more easily and more efficiently when they were present. Upon removal of the hemicelluloses, the cellulose-hemicellulose-cellulose bond was replaced by a more rigid cellulose-cellulose

bond which made the fibers more stress-sensitive and caused failure at lower stress levels.

Centola, et al. (1) suggested that the use of swelling agents to remove hemicelluloses could cause changes in fiber structure even if not shown by x-ray analysis. He felt that a rearrangement of the macromolecules without change in the crystal structure could take place when they regroup after enjoying more freedom of movement under the influence of swelling agents.

It is apparent from the above that considerably more knowledge of the structure of the fiber is required to interpret changes in strength brought about by pulping, bleaching, or other treatments, even within one wood species. Future work should include more complete chemical characterization, not only of the total composition of the fibers but also of the distribution of the various components. Evaluations of strength should recognize the "Jentzen effect" and its impact on strength, and techniques for characterization of the orientation effects in the fiber should also be considered.

ACKNOWLEDGMENTS

The work reported above was carried out in accordance with the first phase of the research program developed by Harry Wilder and Howard Gardner, as described in the proposal dated May 21, 1964. The experimental work was initiated by Edward Daleski assisted by Harry Grady, and subsequent analytical, x-ray, viscosity, and strength measurements were made in several laboratories at the Institute. Particular appreciation is due to Hugh Corbett for assistance in assembling the data and to B. L. Browning, Kyle Ward, Dale Williams, and Norman Thompson for their advice and assistance in interpreting the data.

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